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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification [6] :
C23C 28/00, 28/04, 14/02, 14/08

A1

(11) International Publication Number: WO 96/34128

(43) International Publication Date: 31 October 1996 (31.10.96)

(21) International Application Number: PCT/EP96/01564

(22) International Filing Date: 12 April 1996 (12.04.96)

(30) Priority Data:
08/428,452 25 April 1995 (25.04.95) US

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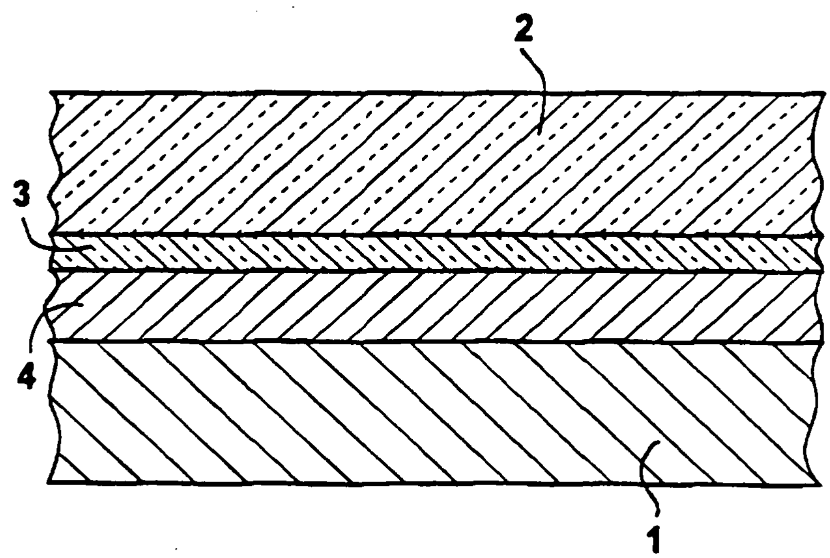
(81) Designated States: CN, CZ, JP, KR, RU, SG, UA, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: METAL SUBSTRATE WITH AN OXIDE LAYER AND AN ANCHORING LAYER

(57) Abstract

An anchoring layer (3) is disposed on a surface of a substrate (1). The substrate is capable to develop a first oxide on the surface and tightly bonded thereto, the first oxide comprising a first metallic element. Alternatively, the surface is formed of the first oxide. The anchoring layer (3) is formed with a spinel of the first metallic element, a second metallic element and oxygen. A second oxide layer (2), which contains an oxide of the second metallic element, is disposed on the anchoring layer. The anchoring layer (3) is formed on the substrate in a series of process steps, which include: establishing an atmosphere containing oxygen around the article; evaporating a compound of the first metallic element and a compound of the other metallic element into the atmosphere and forming a spinel gas phase containing the first metallic element, the second metallic element and the oxygen; and precipitating the spinel gas phase on the article.



METAL SUBSTRATE WITH AN OXIDE LAYER AND AN ANCHORING LAYER

The invention relates to a metal substrate with a second oxide layer and an anchoring layer disposed therebetween. More specifically, the invention relates to a superalloy substrate with a thermal barrier layer and a layer anchoring the thermal barrier layer onto the substrate.

U.S. Patent Nos. 4,055,705 to Stecura et al.; 4,321,310 to Ulion et al.; and 4,321,311 to Strangman disclose coating systems for gas turbine components made from nickel or cobalt-based superalloys. A coating system described comprises a thermal barrier layer made from ceramic, which in particular has a columnar grained structure, placed on a bonding layer or bond coating which in its turn is placed on the substrate and bonds the thermal barrier layer to the substrate. The bonding layer is made from an alloy of the MCrAlY type, namely an alloy containing chromium, aluminum and a rare earth metal such as yttrium in a base comprising at least one of iron, cobalt and nickel. Further elements can also be present in an MCrAlY alloy; examples are given below. An important feature of the bonding layer is that a thin oxide layer of alumina or a mixture of alumina and chromium oxide, as dependent on particulars of the composition of the MCrAlY alloy, inter alia, is developed on the MCrAlY alloy in an oxidizing environment below the thermal barrier layer. Accordingly, a bond between the thermal barrier layer and the alumina layer must be provided.

U.S. Patent No. 5,238,752 to Duderstadt et al. discloses a coating system for a gas turbine component which also incorporates a ceramic thermal barrier layer and an bonding layer bonding the thermal barrier layer to the substrate. The bonding layer is made from an intermetallic aluminide compound, in particular a nickel aluminide or a platinum aluminide. The bonding layer also has a thin oxide layer which must serve to anchor the thermal barrier layer.

U.S. Patent No. 5,262,245 to Ulion et al. describes a result of an effort to simplify coating systems incorporating thermal barrier layers for gas turbine components by avoiding bonding layers. To this end, a composition for a superalloy is disclosed which may be used to form a substrate of a gas turbine component and which develops an alumina layer on its outer surfaces under a suitable treatment. That alumina layer is used to anchor a ceramic thermal barrier layer directly on the substrate, eliminating the need for a special bonding layer to be placed between the substrate and the thermal barrier layer.

U.S. Patent No. 5,087,477 to Giggins et al. shows a method for placing a ceramic thermal barrier layer on a gas turbine component by a physical vapor deposition process. That process comprises establishing an atmosphere having a controlled content of oxygen at the component to receive the thermal barrier layer, evaporating compounds with an electron beam and forming a gas phase, and precipitating the gas phase on the compound to form the thermal barrier layer.

U.S. Patent Nos. 5,154,885; 5,268,238; 5,273,712; and 5,401,307 to Czech et al. disclose advanced coating systems for gas turbine components comprising protective coatings of MCrAlY alloys. The MCrAlY alloys disclosed have carefully balanced compositions to give exceptionally good resistance to corrosion and to oxidation, as well as an exceptionally good compatibility (mechanical, chemical) to the superalloys used for the substrates. The basis of the MCrAlY alloys is formed by nickel and/or cobalt. Additions of further elements, in particular silicon and rhenium, are also discussed. Rhenium in particular is shown to be a very advantageous additive. All MCrAlY alloys shown are also very suitable as bonding layers for anchoring thermal barrier layers on gas turbine components. U.S. Patent No. 5,401,307 also contains a survey over compositions of superalloys which are useful for forming gas turbine components.

A standard practice in bonding an oxide layer, in particular a thermal barrier layer, to an article of manufacture is placing an anchoring layer consisting of alumina on the article, either by placing a suitable bonding layer on the article which develops the alumina on its surface under oxidizing conditions or by selecting a material for the article which is itself capable of developing alumina on its surface. The thermal barrier layer is placed on the bonding layer and bonded to the substrate via the anchoring layer.

The thermal barrier layer itself is expediently made from an oxide ceramic, particularly stabilized or partly stabilized zirconia. "Partly Stabilized Zirconia" classifies a family of

preparations containing zirconia as a principal constituent and at least one other compound which is thoroughly mixed with the zirconia and which inhibits the zirconia to change its crystalline properties under thermal cycling. Examples for such other compounds are yttria, calcia, magnesia, ceria and lanthana; to produce the desired effect, these other compounds have to be admixed to the zirconia in amounts up to 10 percent by weight or even more. Examples are available from the cited documents of the state of the art.

Particulars of the bonding of the thermal barrier layer to an anchoring layer consisting essentially of alumina have not yet attained considerable recognition or even discussion from the technicians working in the field. More or less it has been taken for granted that the alumina, being a ceramic itself and being developed as a layer bonded to a suitable metal substrate, would assure bonding between the metal substrate and a thermal barrier layer placed upon the alumina by its mere existence. Heretofore, only an alumina layer has been given consideration to anchor a thermal barrier layer on a superalloy substrate regardless of its declining bonding capability and increasing spalling probability as it grows during operation due to the exposure to an oxidizing environment. Such growth must be expected to occur at a gas turbine component under high thermal load in an oxidizing environment.

Further enquiries by the inventor have turned out that it is not the mere existence of an alumina anchoring layer which bonds a thermal barrier layer placed thereon thereto, but

that it is a solid state chemical reaction occurring between the alumina and the thermal barrier layer which creates a thin mixing zone between the anchoring layer and the thermal barrier layer where compounds formed from both the anchoring layer and the thermal barrier layer provide for bonding.

It is accordingly an object of the invention to provide a metal substrate with an oxide layer and an improved anchoring layer, which overcomes the above-mentioned disadvantages of the heretofore-known devices and methods of this general type and improves the bonding of the oxide layer, particularly a ceramic thermal barrier layer, to a substrate through an anchoring layer by modifying the anchoring layer in a suitable manner.

With the foregoing and other objects in view there is provided, in accordance with the invention, an article of manufacture, comprising: a metal substrate having a surface and being capable to develop a first oxide layer on the surface and tightly bonded thereto, the first oxide layer comprising a first metallic element; an anchoring layer disposed on the substrate, the anchoring layer comprising a spinel formed with the first metallic element, a second metallic element and oxygen; and a second oxide layer disposed on the anchoring layer, the second oxide layer containing an oxide of the second metallic element.

With the foregoing and other objects in view there is also provided, in accordance with the invention, an article of manufacture, comprising: a substrate having a surface formed

by a first oxide which comprises a first metallic element; an anchoring layer comprising a spinel formed with the first metallic element, a second metallic element and oxygen; and a second oxide layer disposed on the anchoring layer and bonded to the surface by the anchoring layer, the second oxide layer containing an oxide of the second metallic element.

In accordance with an added feature of the invention, the anchoring layer comprises the spinel as a principal constituent, or it consists essentially of the spinel.

In accordance with an additional feature of the invention, the second metallic element is zirconium, and the second oxide layer may contain zirconia as a principal constituent, and particularly, the second oxide layer consists essentially of a partly stabilized zirconia.

In accordance with a further feature of the invention, the anchoring layer is doped with nitrogen, preferably in an amount between 1 and 10 atom percent.

In accordance with again an additional feature of the invention, the substrate is formed of a nickel or cobalt-based superalloy. It is thereby particularly advantageous if a bonding layer is interposed between the substrate and the anchoring layer. The bonding layer is preferably formed of a material selected from the group consisting of metal aluminides and MCrAlY alloys, and it has a preferable thickness of less than 25 micrometers.

In a preferred embodiment, the substrate, the anchoring layer and the second oxide layer together form a gas turbine component. Such a component comprises in particular a mounting portion for holding the component in operation and an active portion subject to a hot gas stream streaming along the component in operation, the active portion being at least partly covered by the anchoring layer and the second oxide layer.

With the above-mentioned and other objects in view there is also provided, in accordance with the invention, a method of bonding a second oxide layer to an article of manufacture formed of a metal substrate having a surface and being capable to develop a first oxide layer tightly bonded to the surface, the first oxide layer comprising a first metallic element, the method which comprises:
placing an anchoring layer on the surface, the anchoring layer comprising a spinel formed with the first metallic element, the second metallic element and oxygen; placing the second oxide layer on the anchoring layer; and bonding the second oxide layer to the substrate via the anchoring layer.

With the above-mentioned and other objects in view there is also provided, in accordance with the invention, a method of bonding a second oxide layer comprising a second metallic element to an article of manufacture which comprises a substrate having a surface formed by a first oxide which comprises a first metallic element, the method which comprises: placing an anchoring layer on the surface, the anchoring layer comprising a spinel formed with the first

metallic element, the second metallic element and oxygen; placing the second oxide layer on the anchoring layer; and bonding the second oxide layer to the substrate via the anchoring layer.

In accordance with an added mode of the invention, the step of bonding the second oxide layer to the substrate is effected by subjecting the substrate with the various layers placed thereon to a suitably selected elevated temperature. Thereby, solid state chemical reactions are effected at respective boundaries between a layer and the substrate or between two layers, creating the desired bonds. Eventually, that subjecting to the elevated temperature can be performed concurrently with the step of placing the second oxide layer.

In accordance with yet an added mode of the invention, the anchoring layer is placed by: establishing an atmosphere containing oxygen around the article; evaporating a compound of the first metallic element and a compound of the second metallic element into the atmosphere and forming a spinel gas phase containing the first metallic element, the second metallic element and the oxygen; and precipitating the spinel gas phase on the article.

The compound of the first metallic element to be evaporated is preferably selected from the group consisting of the first metallic element itself and an oxide of the first metallic element. The compound of the second metallic element is preferably an oxide of the second metallic element.

In accordance with again a further mode of the invention, the compound of the first metallic element and the compound of the second metallic element are evaporated by irradiating at least one solid target containing the respective compound with an electron beam.

In a further development of the invention, the anchoring layer is placed with the following steps: initially establishing the atmosphere containing oxygen at a given partial pressure; and evaporating the compound of the first metallic element and the compound of the second metallic element, forming the spinel gas phase and precipitating the spinel gas phase on the article while concurrently lowering the partial pressure of the oxygen in the atmosphere. The second oxide layer may be placed as follows: establishing another atmosphere containing oxygen around the article; evaporating a compound with the second metallic element and forming an oxide gas phase; precipitating the oxide gas phase on the anchoring layer; and reacting the anchoring layer with oxygen from the atmosphere and oxygen from the oxide gas phase precipitating on the anchoring layer.

In accordance with yet a further mode of the invention, the step of placing the second oxide layer comprises evaporating a compound with the second metallic element and forming an oxide gas phase; and precipitating the oxide gas phase on the anchoring layer.

In accordance with a concomitant mode of the invention, the step of placing the anchoring layer comprises doping the

anchoring layer with nitrogen. Thereby, the anchoring layer is made an efficient diffusion barrier to prevent migration of diffusion active elements through the anchoring layer into the second oxide layer. The doping can in particular be performed by placing the anchoring layer by PVD or a similar process in an atmosphere containing an amount of nitrogen or by heat treating the anchoring layer after its placing in an atmosphere containing nitrogen to diffuse nitrogen into the anchoring layer.

Other features which are considered as characteristic for the invention are set forth in the appended claims.

Although the invention is illustrated and described herein as embodied in a metal substrate with an oxide coating and an improved anchoring layer, it is nevertheless not intended to be limited to the details shown, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

The construction of the invention, however, together with additional objects and advantages thereof will be best understood from the following description of the specific embodiment when read in connection with the accompanying drawings. In the drawings:

Fig. 1 is a fragmentary cross-sectional view of a substrate with a protective coating system incorporating a second oxide layer and an anchoring layer; and

Fig. 2 is a perspective view of a gas turbine airfoil component comprising the substrate and the protective coating system shown in Fig. 1.

Referring now to the figures of the drawing in detail and first, particularly, to Fig. 1 thereof, there is seen a substrate 1 of an article of manufacture, in particular a gas turbine component, which in operation is subject to a heavy thermal load and concurrently to corrosive and erosive attack, including an attack by oxidation. The substrate 1 is formed of a material which is suitable to provide strength and structural stability when subjected to a heavy thermal load and eventually an additional mechanical load by severe forces like centrifugal forces. A material which is widely recognized and employed for such a purpose in a gas turbine engine is a nickel or cobalt-based superalloy.

In order to limit the thermal load imposed on the substrate 1, it has a thermal barrier layer in the form of a second oxide layer 2 placed thereon. This second oxide layer 2 is made from a columnar grained oxide ceramic, in particular consisting essentially of a stabilized or partly stabilized zirconia as explained above. The second oxide layer 2 is anchored to the substrate 1 by means of an anchoring layer 3. This anchoring layer 3 is developed on a bonding layer 4 which has to be placed on the substrate 1 priorly. The bonding layer 4 consists of an MCrAlY alloy and preferably of an MCrAlY alloy as patented in one of the US Patents 5,154,885, 5,268,238, 5,273,712 and 5,401,307. The drawing is

not intended to show the thicknesses of the layers 3 and 4 to scale; the thickness of the anchoring layer 3 might in reality be very much less than the thickness of the bonding layer 4 and amount only to a few layers of atoms, as specified hereinabove.

The anchoring layer 3 consists essentially of a spinel formed with a first metallic element, namely aluminum, and a second metallic element whose oxide constitutes at least partly the second oxide layer 2. That spinel is chemically and crystallographically affine to the material forming the second oxide layer 2 as well as to the material forming the portion of the article located immediately below the anchoring layer 3, namely the bonding layer 4 which in its turn is affine to alumina due to its capability to develop an alumina layer tightly bonded to it, or an alumina layer tightly bonded to the bonding layer 4 and developed thereon under exposure to an oxidizing environment. Thus, the anchoring layer 3 forms a preferred interface between the oxide layer 2 and the part of the article located below the anchoring layer 3, in the embodiment shown the bonding layer 4 resp. an alumina layer emerging from the bonding layer 4 under oxidizing conditions.

The anchoring layer 3 can in particular be placed by a physical vapor deposition (PVD) process, preferably by electron beam PVD and in an oxygen-containing atmosphere. Such a process is in particular carried out while holding the substrate 1 at a temperature of about 700°C. Furthermore, it may be advantageous to place the anchoring layer 3 with an

oxygen deficiency and react that anchoring layer 3 with additional oxygen during placing of the second oxide layer 2, which is then to be done in another atmosphere containing oxygen.

Most preferred is a mode of placing the anchoring layer 3 by precipitating a few layers of atoms with an almost stoichiometric composition and placing the rest of the anchoring layer 3 with an oxygen deficiency. This is expediently done by initially providing an atmosphere which is relatively rich in oxygen, preferably complying with the specification given above. The presence of oxygen in a relatively high amount gives rise to chemical reactions with the constituents of the material located immediately below the anchoring layer 3, thus providing a tight bonding of the anchoring layer 3. Subsequently, the oxygen content of the atmosphere is lowered, particularly by reducing the total pressure of the atmosphere. The oxygen deficiency in the anchoring layer 3 thus occurring is relieved afterwards by a chemical reaction with the constituents of the second oxide layer 2 and with oxygen provided as the second oxide layer 2 is placed. This gives a tight bond to the second oxide layer 2 as well. The thickness of the anchoring layer 3 is preferably kept below 25 micrometers (μm).

The second oxide layer 2 may be placed on the anchoring layer 3 immediately after placing the anchoring layer 3, and in particular by making use of previously used apparatus to the largest possible extent. This may apply in particular if the second oxide layer 2 is also placed by PVD.

The placing of the second oxide layer 2 by means other than PVD is of course also possible. In particular, it is possible to place the second oxide layer 2 by atmospheric plasma spraying.

As a further improvement, it is also contemplated to dope the anchoring layer 3 with nitrogen, thereby providing a nitrogen content between 1 and 10 atom percent, particularly between 2 and 5 atom percent. The nitrogen provides certain slight charge imbalances and spatial distortions in the spinel crystal lattice and thereby renders the spinel opaque or impenetrable for other elements. Thereby, transmission of diffusion active elements like hafnium, titanium, tungsten and silicon from the substrate 1 or the bonding layer 4 into the second oxide layer 2 can be prevented. That measure is particularly suitable if the second oxide layer 2 is a zirconia compound, since almost every zirconia compound must have an admixture of a further compound to stabilize its pertinent properties. Further elements penetrating into the zirconia compound might well impart the stabilization and thus question its long term efficiency, particular when used as a thermal barrier layer. The nitrogen doping of the anchoring layer 3 is well suited to ensure a long term efficiency of the second oxide layer 2. The nitrogen doping of the anchoring layer 3 can be provided concurrently with its placing, particularly by PVD in an atmosphere which contains an efficient amount of nitrogen. In this context, all PVD processes just described are applicable, by using atmospheres containing nitrogen besides oxygen. It is also

possible to dope the anchoring layer 3 after its placing, particularly by a heat treatment in an atmosphere containing an efficient amount of nitrogen and diffusing the nitrogen into the anchoring layer 3.

Fig. 2 shows the whole gas turbine component, namely a gas turbine airfoil component 5, in particular a turbine blade. The component 5 has an airfoil portion 6, which in operation forms an "active part" of the gas turbine engine, a mounting portion 7, at which the component 5 is fixedly held in its place, and a sealing portion 8, which forms a seal together with adjacent sealing portions of neighboring components to prevent an escape of a gas stream 9 flowing along the airfoil portion 6 during operation.

The location of the arrangement shown in Fig. 1 is indicated by the section line I-I.

Referring again to Fig. 1, particular advantages of the novel combination of the anchoring layer 3 and the second oxide layer 2 can be summarized as follows: The anchoring layer 3 has a composition which has similarities to the second oxide layer 2 as well as to the bonding layer 4 and is tightly bonded to both layers by solid-state chemical reactions. It provides for a smooth and graded transition between the material of the second oxide layer 2 and an alumina layer developing between the anchoring layer 3 and the substrate 1 or the bonding layer 4 and yet retains the tight bonds provided by the solid-state reactions. The anchoring layer 3 can be deposited independently from the second oxide layer 2.

Oxidizing the substrate 1 or the bonding layer 4 eventually deposited thereon prior to putting the component to operation can be avoided, thereby lengthening the available lifetime of the component considerably. The combination of the anchoring layer 3 and the second oxide layer 2 thus made has all advantages of such combinations known from the prior art and additionally features a substantially prolonged lifetime.

Claims

An article of manufacture, comprising:
a metal substrate having a surface and being capable to develop a first oxide layer on said surface and tightly bonded thereto, said first oxide layer comprising a first metallic element;
an anchoring layer disposed on said surface, said anchoring layer comprising a spinel formed with said first metallic element, a second metallic element and oxygen; and
a second oxide layer disposed on said anchoring layer, said second oxide layer containing an oxide of said second metallic element.

2. An article of manufacture comprising
a substrate having a surface formed by a first oxide which comprises a first metallic element;
an anchoring layer disposed on said surface, said anchoring layer comprising a spinel formed with said first metallic element, a second metallic element and oxygen; and
a second oxide layer disposed on said anchoring layer and bonded to said surface by said anchoring layer, said second oxide layer containing an oxide of said second metallic element.

3. The article according to claim 1 or claim 2, wherein said anchoring layer comprises said spinel as a principal constituent.

4. The article according to claim 1 or claim 2, wherein said anchoring layer consists essentially of said spinel.

5. The article according to one of the preceding claims, wherein said first metallic element is aluminum.

6. The article according to one of the preceding claims, wherein said second metallic element is zirconium.

7. The article according to claim 6, wherein said second oxide layer contains zirconia as a principal constituent.

8. The article according to claim 6, wherein said second oxide layer consists essentially of a partly stabilized zirconia.

9. The article according to one of the preceding claims, wherein said anchoring layer is doped with nitrogen.

10. The article according to claim 9, wherein said nitrogen is present in said anchoring layer in an amount between 1 and 10 atom percent.

11. The article according to one of the preceding claims, wherein said substrate is formed of a nickel or cobalt-based superalloy.

12. The article according to one of the preceding claims, comprising a metallic bonding layer interposed between said substrate and said anchoring layer.

13. The article according to claim 12, wherein said metallic bonding layer is formed of a material selected from the group consisting of metal aluminides and MCrAlY alloys.

14. The article according to one of the preceding claims, wherein said anchoring layer has a thickness of less than 25 micrometers.

15. The article according to one of the preceding claims, wherein said substrate, said anchoring layer and said second oxide layer form a gas turbine component.

16. The article according to claim 15, wherein said gas turbine component comprises a mounting portion for holding the component in operation and an active portion subject to a hot gas stream streaming along the component in operation, said active portion being at least partly covered by said anchoring layer and said second oxide layer.

17. A method of bonding a second oxide layer comprising a second metallic element to an article of manufacture formed of a metal substrate having a surface and being capable to develop a first oxide layer tightly bonded to said surface, said first oxide layer comprising a first metallic element, the method which comprises:

placing an anchoring layer on the surface, the anchoring layer comprising a spinel formed with the first metallic element, the second metallic element and oxygen;

placing the second oxide layer on the anchoring layer; and

bonding the second oxide layer to the substrate via the anchoring layer.

18. A method of bonding a second oxide layer comprising a second metallic element to an article of manufacture comprising a substrate having a surface formed by a first oxide which comprises a first metallic element, the method which comprises:
placing an anchoring layer on said surface, the anchoring layer comprising a spinel formed with the first metallic element, the second metallic element and oxygen;
placing the second oxide layer on the anchoring layer; and
bonding the second oxide layer to the substrate via the anchoring layer.

19. The method according to claim 17 or claim 18, wherein the step of bonding the second oxide layer to the substrate comprises subjecting the substrate with the layers placed thereon to an elevated temperature.

20. The method according to one of claims 17 to 19, wherein the step of placing the anchoring layer comprises:
establishing an atmosphere containing oxygen around the article;
evaporating a compound of the first metallic element and a compound of the second metallic element into the atmosphere and forming a spinel gas phase containing the first metallic element, the second metallic element and the oxygen; and
precipitating the spinel gas phase on the article.

22. The method according to claim 20 oder claim 21, which comprises evaporating the compound of the second metallic element as selected to be an oxide of the second metallic element.

23. The method according to one of claims 20 to 22, which comprises evaporating at least one of the compound of the first metallic element and the compound of the second metallic element by irradiating at least one solid target containing the respective compound with an electron beam.

24. The method according to one of claims 20 to 23, wherein the step of placing the anchoring layer comprises:
initially establishing the atmosphere containing oxygen at a given partial pressure; and
evaporating the compound of the first metallic element and the compound of the second metallic element, forming the spinel gas phase and precipitating the spinel gas phase on the article while concurrently lowering the partial pressure of the oxygen in the atmosphere;
and wherein the step of placing the second oxide layer comprises:
establishing another atmosphere containing oxygen around the article;
evaporating a compound with the second metallic element and forming an oxide gas phase;
precipitating the oxide gas phase on the anchoring layer; and
reacting the anchoring layer with oxygen from the atmosphere and oxygen from the oxide gas phase precipitating on the anchoring layer.

evaporating a compound with the second metallic element and forming an oxide gas phase;
precipitating the oxide gas phase on the anchoring layer; and reacting the anchoring layer with oxygen from the atmosphere and oxygen from the oxide gas phase precipitating on the anchoring layer.

25. The method according to one of claims 17 to 24, wherein the step of placing the second oxide layer comprises evaporating a compound with the second metallic element and forming an oxide gas phase, and precipitating the oxide gas phase on the anchoring layer.

26. The method according to one of claims 17 to 25, wherein the step of placing the anchoring layer includes doping the anchoring layer with nitrogen.

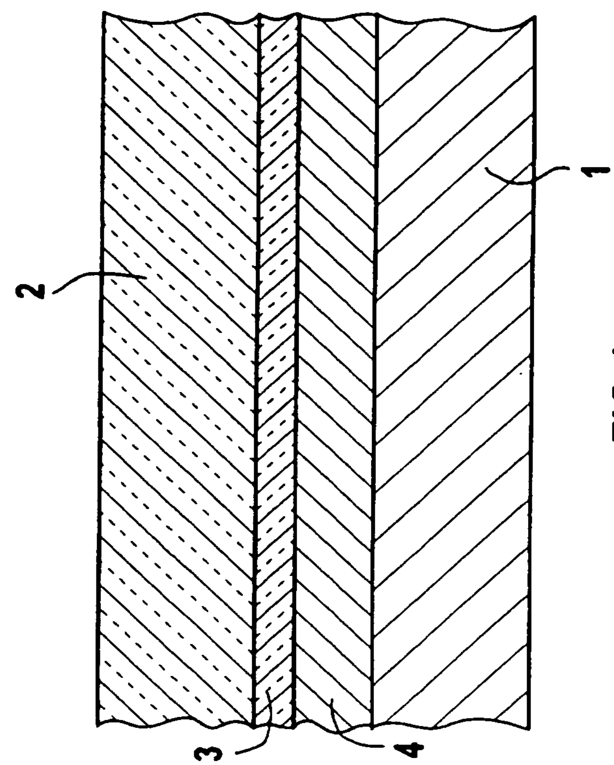


FIG 1

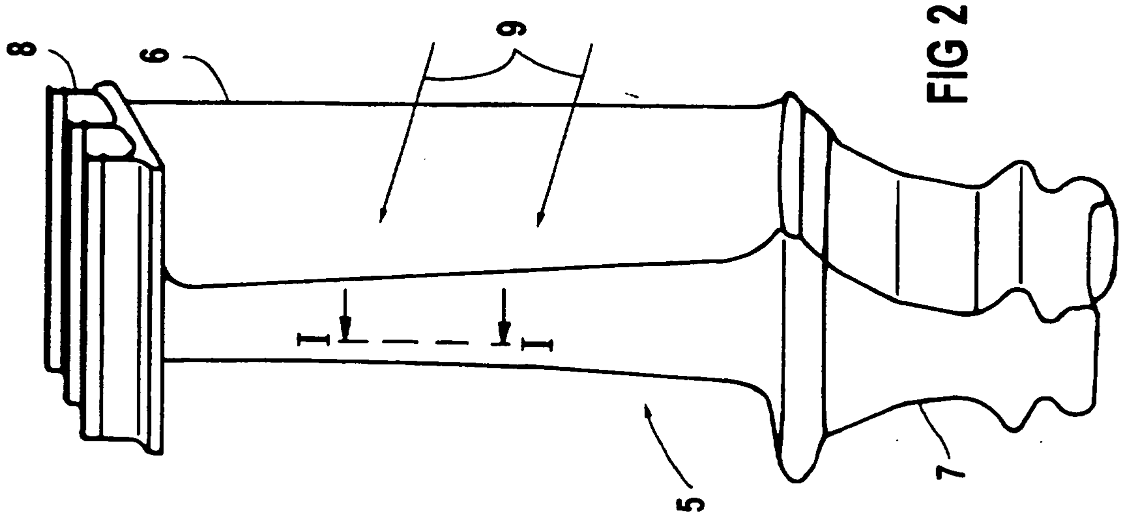


FIG 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 96/01564

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23C28/00 C23C28/04 C23C14/02 C23C14/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C23C F01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 013, no. 095 (C-573), 6 March 1989 & JP,A,63 274751 (TOYOTA MOTOR CORP), 11 November 1988,	1-4,17, 18
Y	see abstract	5-8, 11-16,19

Y	GB,A,2 159 838 (UNITED TECHNOLOGIES CORP) 11 December 1985 see page 2, line 36 - line 109	5-8, 11-16,19

A	US,A,5 262 245 (ULION NICHOLAS E ET AL) 16 November 1993 see examples 1-4	1-26

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

I

Date of the actual completion of the international search	Date of mailing of the international search report
26 July 1996	08.08.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Ekhult, H

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	NINTH INTERNATIONAL CONFERENCE ON METALLURGICAL COATINGS AND PROCESS TECHNOLOGY, SAN DIEGO, CA, USA, 5-8 APRIL 1982, vol. 95, no. 1, ISSN 0040-6090, THIN SOLID FILMS, 3 SEPT. 1982, SWITZERLAND, pages 3-20, XP002009109 GRUNLING H W ET AL: "The role of silicon in corrosion-resistant high temperature coatings" see page 4, line 1 - page 5, line 6 ---	1-26
A	THIN SOLID FILMS, 10 MAY 1985, SWITZERLAND, vol. 127, no. 1-2, ISSN 0040-6090, pages 93-105, XP002009110 STRANGMAN T E: "Thermal barrier coatings for turbine airfoils" see page 101, line 4 - line 9; figure 7 ---	1-26
A	EP,A,0 494 389 (WESTINGHOUSE ELECTRIC CORP) 15 July 1992 see page 5, line 6 - line 22; figure 3 ---	1-26
A	EP,A,0 185 603 (UNITED TECHNOLOGIES CORP) 25 June 1986 see claims 1,2 ---	1-26
A	W. BEELE: "PVD-(PHYSICAL VAPOR DEPOSITION) SCHICHTENTWICKLUNGEN FÜR HOCHTEMPERATURANWENDUNGEN IN THERMISCHEN MASCHINEN" 1994 , VDI VERLAG , DE XP002009111 see page 85, line 8 - page 87, line 17 -----	1-26

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 96/01564

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